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Diamagnetism of Organic Liquid Mixtures.

By

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Abstract.

The magnetic susceptibilities of some organic liquid mixtures have been examined by a new method. It is found that there are no departures from the additive law of mixtures. The cases of acetone-chloroform and acetone-nitrobenzene mixtures are examined critically and strong evidence is put forward to show that association does not produce any change in the specific diamagnetic susceptibility.

1. *Introduction.*

This paper is a continuation of a previous paper on this subject by the writer and Sivaramakrishnan.[1] A large amount of work has been accomplished recently on the diamagnetism of mixtures of organic liquids. Unfortunately however reports are not unanimous regarding the behaviour of such mixtures from the point of view of the additive law of magnetic susceptibilities. Taking a mixture like acetone and chloroform, Ranganadham,[2] Buchner,[3] Trew and Spencer,[4]

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[1] Ind. Jour. Phys., 6, 509 (1932).

[2] Nature, 127, 975 (1931); Ind. Jour. Phys., 6, 421 (1932).

[3] Nature, 128, 302 (1931); Zeits. f. Phys., 72, 344 (1931).

[4] Nature, 129, 95 (1932).

Farquharson[5] and Sibaiya and Venkataramiah[6] have shown that there are 2 to 5 per cent. variations from the additive law at intermediate concentrations. Their experiments (except those of Trew and Spencer and Farquharson) were conducted by noting the rise in a Quincke's apparatus except in the last instance where the growth of drops and oscillations of a plate in inhomogeneous magnetic fields were studied. In all these experiments, we do not know how far surface tension plays a part but attempts made by Sivaramakrishnan and the writer to study the influence of magnetic fields on the surface tensions of organic liquids gave a negative result.* While this interesting point will be discussed at length later in the paper, we may here mention that the actual shapes of the curves of these investigators do not show any common resemblance whatever. Further while the above writers, except Buchner, obtain a maximum *decrease* in the specific diamagnetic susceptibility (χ) at about 30% of acetone in the mixture, Trifonov[7] and Buchner[9] at the same concentration obtain an *increase* in value. Further Garssen[8] using a Curie-Cheneveau balance obtains an increase of nearly 17% in the specific diamagnetic susceptibility of mixtures of acetone and nitrobenzene. Such a result is difficult to account for from a theoretical point of view. Kido[9] more recently reports that in all the liquid mixtures investigated by him, there were no departures from the additive law and that diamagnetic susceptibilities are not affected by association.

The question is of fundamental interest in the theory of magnetism since it raises the problem of the variation of magnetic properties of the molecule which possesses a dipole

5   Nature, 129, 25 (1932).

6   Ind. Jour. Phys., 7, 393 (1932).

*   See Rolton and Troop, Proc. Phys. Soc., 36, 205 (1924).

7   Tables Ann. Int. de Const., 7, 1014 (1931).

8   Comptes Rendus, 196, 541 (1933).

9   Sci. Rep. Tohoku Imp. Uny., 21, 385 (1932).

moment in the presence of another molecule also carrying a dipole moment. It was therefore felt that it would be of interest if the measurements are made by a different method.

2. *Experimental Method.*

The new method is a kind of combination of the Curie and the Guoy methods, the Guoy differential forces being measured by the Curie method. With greater facilities, the method is indeed capable of much greater precision and accuracy. It gives us in fact a direct method of comparing the volume susceptibilities of two liquids.
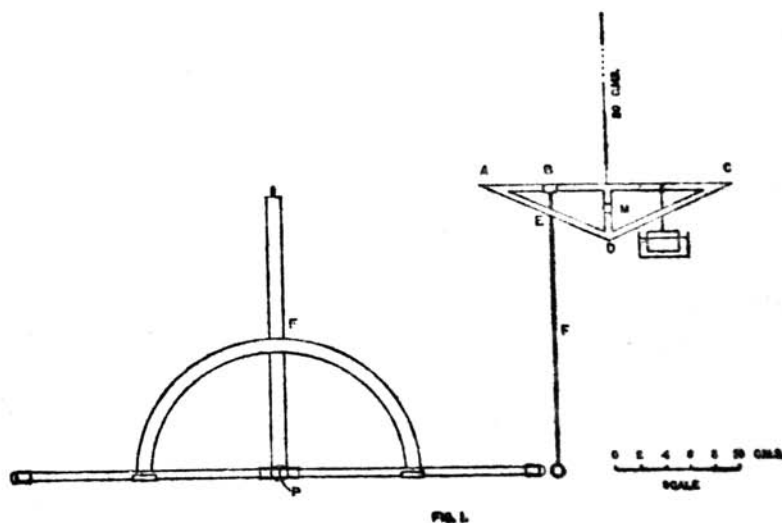
Fig. 1.

ABCD in Fig. 1 is a light aluminium framework suspended from a suspension wire of No. 42 (S.W.G) copper wire of length 30 cms. Another framework F of the same metal (side view also shown in Fig. 1) is rigidly attached to ABCD at BE. This framework carries two glass tubes horizontally. Each of these glass tubes is closed flatly at

one end and has a ground stopper at the other end. They are placed with their axes in the same line and their closed ends touching each other, this junction being arranged to be at the centre of the space between the two polepieces of an electromagnet. A mirror M reflected a beam of light on a scale on which the deflections were read.

The electromagnet used was of the Pye's type and had in these experiments pole faces 1 cm. in diameter and 6·5 mms. apart. The glass tubes used had a uniform and equal diameter, being specially selected for the purpose. The Guoy force on a liquid in one of these tubes depends on the inner area and the square of the magnetic field. Increasing the distance between the polepieces decreases the magnetic field while the area of section of the tube could be increased. Rough preliminary investigations showed that the dimensions used in this investigation gave the largest force for any given magnetic current. The field used was about 11,000 gauss.

The currents were taken from a 120 volt accumulator battery, aud measured on a Cambridge Scientific Instrument Company ammeter reading accurately to one tenth and by estimation to one hundredth of an ampere.

Let us have the two tubes filled with two different liquids having volume susceptibilities k_1 and k_2. If the magnetic field has intensities H and H' at the two ends of any one of the two tubes (which have the same length), the magneto-tractive forces on them are given by $\frac{1}{2}k_1A(H^2-H'^2)$ and $\frac{1}{2}k_2A(H^2-H'^2)$.[*] If both the liquids are diamagnetic, the differential force acting on both the tubes fixed to the same framework is the difference between these two expressions and will act in such a direction that the more diamagnetic

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[*] H' was found to be $\frac{1}{300}$% of H and hence has been neglected in the calculation.

liquid will tend to move away from the centre of the volume between the polepieces. To these we should add the differential force on the two glass tubes but since these are constructed to be almost identically the same, this force is very small and in the investigation, this was measured and allowed for directly. The magnetic values of the displaced air mutually cancel out since the volumes of the two tubes are also nearly equal. The differential force $\frac{1}{2}AH^2(k_1 - k_2)$ will produce a couple on the torsion wire and hence give rise to a deflection on the scale.

$$\tfrac{1}{2}AH^2(k_1 - k_2) \propto d$$

where d is the deflection obtained on the scale. Since A and H are maintained constant, the difference of the volume susceptibilities is found to be directly proportional to the deflection. If we take one of the two liquids as a standard, the volume susceptibility of the other is known. If the density of this liquid is known, we can calculate its specific diamagnetic susceptibility.

Great care had to be taken in bringing the tubes always to the same position whenever readings were taken. A telescope was placed with its axis to coincide with that of the tubes and focussed to bring a point on one of the ground caps to the centre of the cross wires in the field of view.

An idea of the sensitiveness obtained in these experiments can be had from the following figures. In the case when the tubes contained acetone and chloroform, a deflection of 26·2 cms. (corrected for differences in the distances of the divisions of the straight scale from the mirror) was obtained. Their volume susceptibilities were found to be 0·7307 and 0·4701 respectively. Thus a difference of about 0·261 in the volume susceptibility was read by a deflection of 262 divisions on the

scale. These readings could be taken to within $\frac{1}{5}$ of a divi_sion. Taking into account the other factors also, it can be safely assumed that the volume susceptibilities in this investigation are correct to within $\frac{1}{25}$ %.

Great care was taken in filling the tubes completely and in weighing them before and after the magnetic experiment. The density values were compared with that of water at the same temperature and then calculated for water at 4°C. The standard of susceptibility was taken to be 0·720 at 20°C.[10]

The liquids were all extra pure Kahlbaum's and were purified by distillation. In the case of acetic acid, it was initially purified by freezing in ice at 16·7°C. The agreement of our density values ($\rho_4{}^{30}$) with the standard measurements shows that our liquids were pure and that the error in our results did not exceed $\frac{1}{5}$ %.

3. Results.

A collection of the results for the different liquids used in this investigation is given below.

The fact that the values of the specific diamagnetic susceptibility of the different liquids agree very well with those obtained by other investigators shows the correctness of the method adopted here.

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[10] All values of specific diamagnetic susceptibility (χ) in this paper are to be multiplied by 10^{-6}. According to Cabrera and Fahlenbrach, (Zeits. f. Phys., 82, 761, 1933) $\chi_{30}/\chi_{20} = 1\cdot0011$. This would give $\chi_{30} = \cdot72079$ and assuming $\rho_4{}^{30} = 0\cdot99567$ (Landolt Bornstein Tabellen, p. 74), κ_{20} works to 0·7177. This was the value adopted in this investigation. However Auer (Ann. der Physik, 18, 609, 1933) gives $\chi_{30} = 0\cdot72258$ which leads to $\kappa_{30} = 0\cdot7194$. N.B. All values of κ and χ in this paper are to be multiplied by 10^{-6}.

TABLE I.

Liquid.	Electric moment. $\times 10^{18}$ [11]	Vol. Susy. k	ρ_4^{30}	χ				Other workers.
				R	R & S	S.P.R.	I.C.T.	
Acetone	2·70	0·4701	0·794	0·592	0·595	0·5971	0·581	0·58*
								0·57**
Chloroform	1·05	0·7307	1·476	0·495	0·494	0·4940	0·488	0·485*
								0·46**
Nitrobenzene	3·90	0·6060	1·200	0·505	0·513	...	0·499	
Benzene	·06	0·6191	·878	0·705	0·702	0·7042	0·712	
Acetic acid	...	0·5408	1·040	0·520	...	...	0·526	0·58**
Aniline	...	0·6979	1·010	0·691	...	...	0·692	

R—Author.   R & S—Rao and Sivaramkrishnan, ref. 1.

S.P.R.—S. P. Ranganadhan, ref. 2.   I.C.T.—International Critical Tables, Vol. 6, p. 361.

* Buchner, ref. 3.

** Sibaiya and Venkataramiah, ref. 6.

In choosing the liquids for the investigation of the additive law, Rao and Sivaramakrishnan were guided by the shapes of the molecules. In this paper, on the other hand, the electric moments of the liquids have been used as the guiding factor. A simple consideration will indicate that if any deviations from the additive law are to be expected at all, they should arise only in the case where the liquids contain molecules having permanent electric moments. Therefore mostly such liquids have been used in this investigation and the results seem to indicate that even in these cases, there are no variations from the additive law.

(a) Acetone and Chloroform.

A reference was made in Sec. 1 to the conflicting results obtained by various workers with this mixture. In spite of

[11] Van Vleck, Theory of Electric and Magnetic Susceptibilities, p. 66.

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careful measurements made in this investigation, no variation
from the additive law was obtained.

TABLE II.—Acetone and Chloroform.

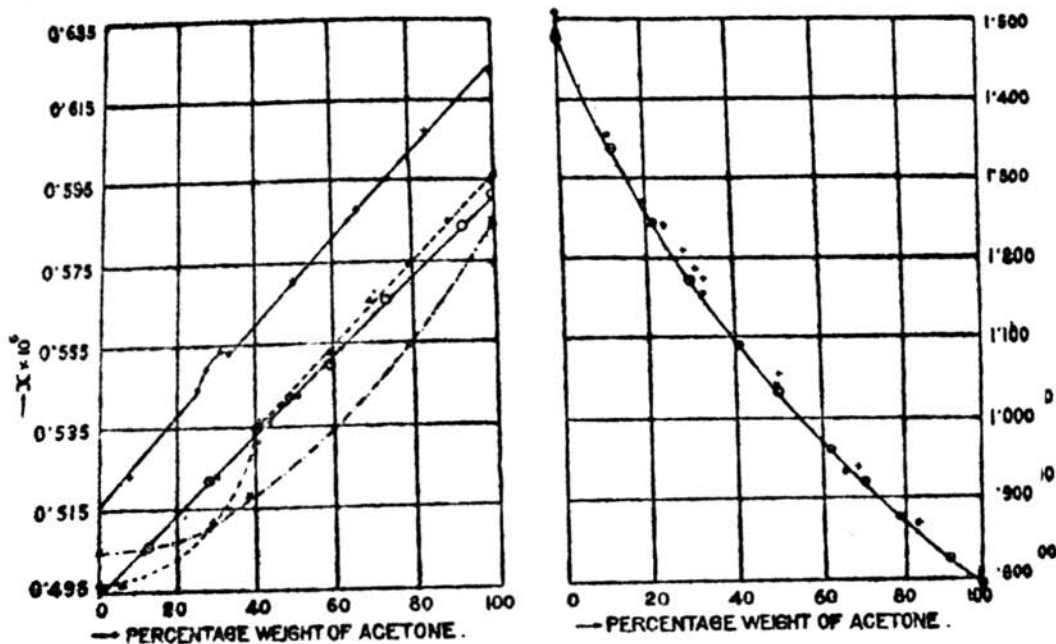| Percentage weight of acetone in the mixture.	ρ_4^{30}	x
0	1·476	0·495
12·5	1·338	0·506
27·8	1·190	0·522
42·7	1·063	0·535
58·1	0·985	0·550
72·2	0·910	0·566
91·8	0·822	0·584
100·0	0·794	0·592

Fig. 2.

A graph between the composition and χ is shown in Fig. 2. It is seen that it is a straight line. Plots are also made of the results of Trifonov,[7] Ranganadham,[2] Sibaiya and Venkataramiah[5] and Rao and Sivaramakrishnan.[1] As was mentioned earlier, it will be noticed that Trifonov and Buchner obtain an increase in χ while Ranganadham and Sibaiya and Venkataramiah obtain a decrease in this value. It will also be noticed that the shapes of the curves of the latter investigators show no mutual agreement.[12] While the results of Rao and Sivaramakrishan were subject to an error not exceeding $\frac{1}{2}\%$, the results of the present investigation are accurate to within $\frac{1}{5}\%$. There do not seem to be any deviations from the additive law to within this limit of error. The density curves of the mixtures are also interesting. It will be noticed that our results agree closely with those of other investigators. The largest departure from the linear relation occurs at a concentration of about 50% of acetone in the mixture by weight and is *not more than* 9%. A fuller discussion will be given in Section 4.

TABLE III.—Acetone and Nitrobenzene.

Precentage weight of acetone in the mixture.	$\frac{30}{\rho_4}$	χ
0	1·200	0·505
15·6	1·11S	0·51S
30·2	1·040	0·531
42·3	0·985	0·542
61·9	0-910	0·5SS
77·2	0·852	0·572
90·2	0·S14	0·5S3
100·0	0·794	0·592

[12] There are variations of as much as 4%, between their results at large concentraions of acetone.

(b) Acetone and Nitrobenzene.

This is a typical mixture since these two types of molecules have the largest dipole moments in the list of liquids studied here. The results are given in Table III.

Fig. 3 shows the graph between the composition and χ. The results of Garssen [8] which are also plotted show considerable departures (as much as 17%) at intermediate concentrations) from the additive law. There are two points in this connection which need careful attention. Firstly, we have an increase in the diamagnetic susceptibility in the case of mixtures. Secondly, the density data do not show any notable anomaly. The deviations in the density-concentration curve shown in Fig. 3 are just similar to what we observe in the case of other liquids. We have to mention also here that the Curie-Cheneveau balance method has been rather disappointing in its application to the measurement of specific susceptibilities and the inconsistency of the plots of Garssen should be attributable to the method used. It will be noted that in the initial experiments of Trew and Spencer [13] they also obtained very inconsistent results with acetone-chloroform mixtures using this method. It is therefore significant that Hoare [14] has recently pointed out the disadvantages of this method in the measurement of specific susceptibilities. Garssen's density measurements, on the other hand, coincide very well with those obtained here.

(c) Acetone and Benzene.

Acetone has a strong electric moment while benzene is almost nonpolar. The results are given below.:

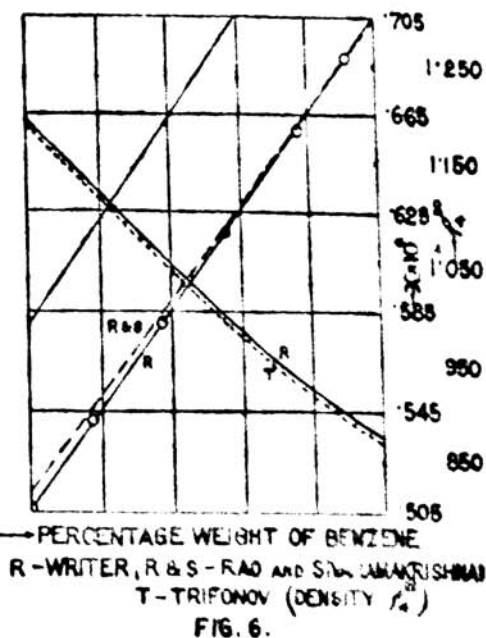[13] Proc. Roy. Soc., A·, 131, 209 (1931).
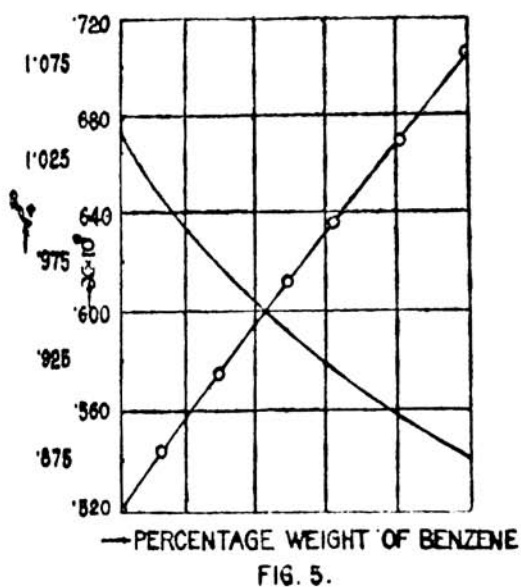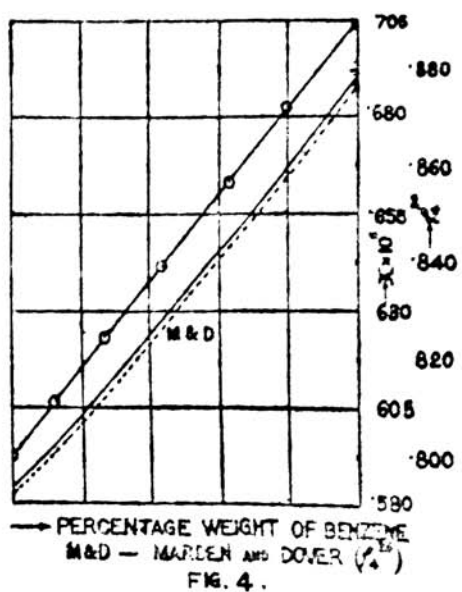[14] Nature, 132, 514 (1933).

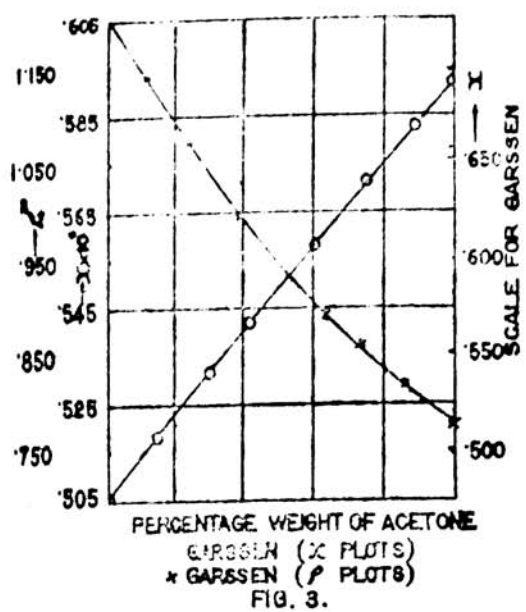PERCENTAGE WEIGHT OF ACETONE
GARSSEN (X PLOTS)
* GARSSEN (ρ PLOTS)
FIG. 3.

PERCENTAGE WEIGHT OF BENZENE
M&D — MARDEN AND DOVER ($\frac{D}{4}$)
FIG. 4.

PERCENTAGE WEIGHT OF BENZENE
FIG. 5.

PERCENTAGE WEIGHT OF BENZENE
R — WRITER, R & S — RAO AND SIVARAMAKRISHNA
T — TRIFONOV (DENSITY $\frac{D}{4}$)
FIG. 6.

TABLE IV.—Acetone and Benzene.

Percentage weight of benzene in the mixture.	ρ^{30}_4	χ
0	0·794	0·592
12·5	0·802	0·605
27·5	0·813	0·622
44·0	0·826	0·640
63·0	0·843	0·661
80·0	0·858	0·682
100·0	0·878	0·705

In Fig. 4 is shown the curve between the concentration of benzene in the mixture and the specific diamagnetic susceptibility. This curve is a straight line while the composition-density curve shows a small deviation from the straight line curve. The results obtained by Marden and Dover [15] are also plotted in the same graph and show a fairly good coincidence with these measurements.

(d) Benzene and Acetic Acid.

Acetic acid shows considerable association in light scattering experiments.[16] A study of the mixtures of this fatty acid with benzene is therefore of interest. Even in this case there is no evidence of any departure from the additive law. The results are tabulated below and the composion-χ and the composition-density curves are shown in Fig. 5. The density variations do not show departures of more than 2% at intermediate concentrations from the corresponding straight line curve.

[15] J. Am. Chem. Soc., 88, 1240, (1916); taken from Tables Ann. Int. de Const., 4, 47 (1921).

[16] Ind. Jour. Phys., 3, 1 (1928).

Table V.—Benzene and Acetic Acid.

Percentage weight of benzene in the mixture.	ρ_4^{30}	χ
0	1·040	0·520
13·2	1·010	0·546
30·0	0·978	0·574
40·0	0·942	0·608
62·5	0·920	0·636
80·8	0·896	0·668
100·0	0·878	0·705

(e) Benzene and Nitrobenzene.

This mixture has been studied by Trifonov[7] and Rao and Sivaramakrishnan.[1] These investigators did not find any departures from the additive law. The same result has been noted in the present work also. The results are given below:—

Table VI.—Benzene and Nitrobenzene.

Percentage weight of benzene in the mixture.	ρ_4^{30}	χ
0	1·200	0·505
17·3	1·130	0·538
37·5	1·054	0·578
56·4	0·996	0·616
77·6	0·934	0·658
91·8	0·896	0·690
100·0	0·878	0·705

It will be noted from the curves given in Fig. 6 that Trifonov's values of χ are uniformly higher than those obtained by Rao and Sivaramakrishnan and by the author.

(f) Acetone and Acetic Acid.

This mixture offers also an interesting study since both are polar. A remarkable result obtained with this mixture is that the density curve is linear. This observation however is not new and has been noticed already.[17] The composition-susceptibility curve is also linear (Fig. 7). The results are given below:

FIG. 7.

FIG. 8.
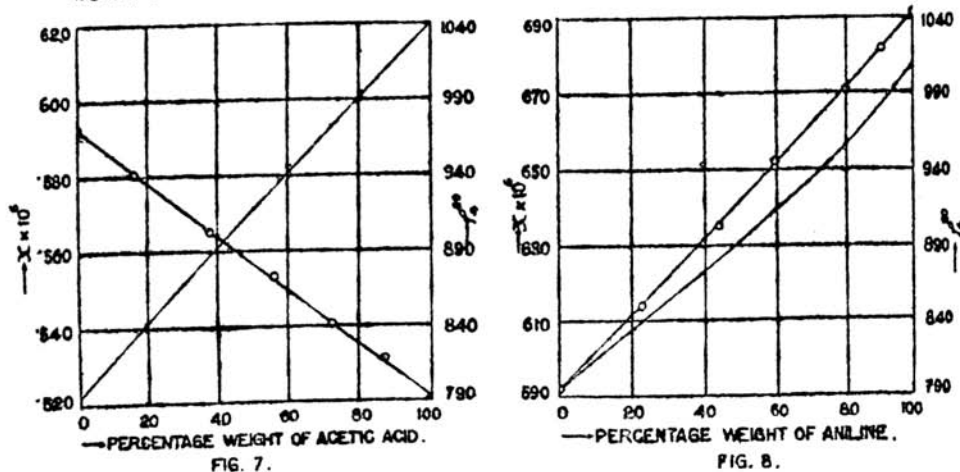
Table VII.—Acetone and Acetic Acid.

Percentage weight of acetic acid in the mixture.	ρ_4^{30}	X
0	0·794	0·592
16·0	0·832	0·580
37·4	0·884	0·565
55·2	0·928	0·553
72·0	0·968	0·540
86·3	1·006	0·531
100·0	1·040	0·520

[17] Tables Ann. Int. de Const., 3, 28 (1914).

(g) Acetone and Aniline.

The curve shown in Fig. 8 between the composition and χ is found to be a straight line. There are also small changes from the linear relation in the C, ρ_4^{30} curve also. The following table gives the results obtained with this mixture :

Table VII.—Acetone and Aniline.

Percentage weight of aniline in the mixture.	ρ_4^{30}	χ
0	0·794	0·592
22·5	0·840	0·614
44·0	0·884	0·635
59·7	0·912	0·652
79·5	0·956	0·671
90·0	0·980	0·682
100·0	1·010	0·691

4. Discussion.

In an extremely interesting paper [18] Kido has studied the magnetic susceptibility of ions. In previous papers [18] he had worked out the ionic susceptibilities in certain important cases and by using these values, he has shown that the molecular susceptibilities of inorganic and organic compounds could be calculated by assuming the additive law. These values agree very satisfactorily with the observed values. It may be recalled that Pascal found that the molecular susceptibility of a compound can be obtained as the sum of the atomic susceptibilities of the atoms of which the molecule of the compound

[18] Sci. Rep. Tohoku Imp. Uny., 21. pp. 149, 288, 869 (1932) ; specially 22, 334 (1933).

is composed. A constant depending on the nature of the molecule had also to be added. Kido has taken the calculation a bit further and by using appropriate ionic susceptibilities has dispensed with the constant of Pascal. The additive law may thus be taken as definitely established.

In the light of these observations, it is difficult to account for any variations from the additive law in the case of mixtures except by a chemical reaction between the two types of molecules in which the nature of the bond is completely altered. Such a chemical action will be accompanied by certain anomalies in the physical properties of the mixtures at those concentrations for which the action is strongest. In the density curves of the mixtures of acetone and chloroform and of acetone and nitrobenzene, no such anomalies have been noted. The density curves resemble exactly those which are obtained in the cases of liquids which have no mutual action.

Sibaiya and Venkataramiah[5] have studied the variation of the viscosity and vapour pressure with composition. It is doubtful whether we can call these facts for support in the variation of magnetic susceptibilities. The viscosity diagrams of mixtures show that they are sensitive to temperatures. A reference to the work of Faust[19] indicates that as the temperature of the acetone-chloroform mixture is raised from 13°C to 39°C, the concentration of chloroform in the mixture at which the maximum coefficient of viscosity occurs passes gradually from 82% to larger values ; at 19°C, the curve is almost a straight line and at 39°C, the curve becomes straight. The vapour pressures of the mixtures are guided by the relative molecular concentrations of the liquids.

The case of acetic acid studied by Sibaiya and Venkataramiah is different since in this case a distinct hump is formed in the composition-susceptibility curve at a composition corresponding to equal molecular concentrations of acetic acid

[19] Tables Ann. Int. de Const., 3, 47 (1914).

and water and a *change* in the nature of the carbon link occurs in the chemical action.

There are two methods by which it is possible to explain the discordance of the results obtained by us and other workers. First it is just possible that temperature may have a predominant part to play and that if experiments are conducted at higher temperatures the variations from the additive law may disappear. We presume here that the temperatures at which we have made measurements are higher than those of the other workers ; and since the mixing of acetone and chloroform is accompanied by evolution of heat, increase of temperature would mean less number of molecules combining with each other. We have instituted careful experiments to study how the susceptibilities of the mixtures of acetone and chloroform vary with temperature (Ref. 25).

But judging from what we have set forth at the beginning of this section, particularly based on Kido's calculations, it is very unlikely that there will be any such variations.

A second and perhaps more interesting possibility is that the variations are due to the Quincke method itself or to the methods in which surfaces of liquids are involved. There is much evidence to show that while surface methods appear to give the variations noted, Curie methods do not. Mention may here be made of similar discrepancies in the study of the temperature variation of the susceptibilities of liquids. In the case of nitrobenzene, Mathur[20] found that between 15° and 75°C, the specific susceptibility decreases from ·502 to ·469. Rao and Sriraman[21] found that between 30° and 110°C, the diamagnetic susceptibility decreases at first, attains a minimum at about 75°C and then rises gradually. These investigators used the Quincke method. On the other hand, Cabrera and Fahlenbrach,[22] using the Curie method, showed

[20] Ind. Jour. Phys., 6, 207 (1931).

[21] Ind. Jour. Phys., 8, 315 (1934).

[22] Zeits. f. Phys., 85, 568 (1933).

that the diamagnetism of nitrobenzene in the liquid was independent of temperature below about 100°C. It was suggested in the paper by Rao and Sriraman that the fall in the range from 30° to 70°C might be due to the gradual breaking up of association. A more careful consideration indicates that even in the case of nitrobenzene, association may not produce any change in the specific diamagnetic susceptibility. Todd [23] very recently found that the changes in the X-ray diffraction pattern of nitrobenzene produced by increase of temperature and circulation substantiated the assumption that the nitrobenzene molecules associate in pairs and are dissociated by thermal or mechanical agitation. The structural chemical formula of nitrobenzene has been considered at some length by Todd. Smyth has shown that the electric moment of the nitrobenzene molecule lies in the plane of the benzene ring, the NO_2 group being negative with respect to the benzene ring. When two molecules therefore associate to form a double melecule, the dipoles of the single molecules oppose and cancel each other. Thus there are no electron linkages or co-ordinate links between the molecules but only electrostatic interaction. It is obvious therefore that such a state of association would not give rise to any change in the diamagnetic susceptibility but would profoundly affect the properties like optical and X-ray scattering, electric and magnetic double refraction [24] and the Faraday rotation. The results of Rao and Sriraman on the temperature effect of the diamagnetism of nitrobenzene were obtained as early as in the summer of 1932 but these considerations stood in the way of their publication earlier. It is therefore of great interest to find that Cabrera and Fahlenbrach found no variation in the diamagnetic specific susceptibility of nitrobenzene as the temperature of the liquid was raised. Here again it appears to the writer that the Quincke method is responsible

[23] Phys. Rev., 4, 44, 787 (1933).

[24] Comp. Rend., 197, 1612 (1983).

for the variations observed by Mathur, and by Rao and Sriraman.[25]

When it is admitted that nitrobenzene does not show any change in the value of its specific diamagnetic susceptibility due to association, it is difficult to see how binary mixtures of nitrobenzene with other liquids would show variations from the additive law. If, further, this variation depends on the electric moment of the other molecule, then there should be a progressive change as the electric moment of the other type of molecule is reduced by taking different suitable liquids. Such a progressive change has not been noted in this investigation.

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[25] *Note added in proof* 21 5.34 :—More recently, P. S. Varadachari has studied in this laboratory in an extremely careful manner, the variation with temperature of the diamagnetic susceptibilities of pure organic liquids and their binary mixtures. He used the Quincke method with large magnetic fields. When all the corrections are applied, it is found that the additive law is obeyed at different temperatures in the case of typical mixtures like *acetone* and *chloroform* and *acetone* and *nitrobenzene*. No variation of the diamagnetic susceptibility of nitrobenzene with temperature was obtained. The presence of impurities in the liquids and of air above them affected the results considerably.